

# Ni–Cu ion exchange observed for Ni(II)–porphyrins on Cu(111)<sup>†</sup>

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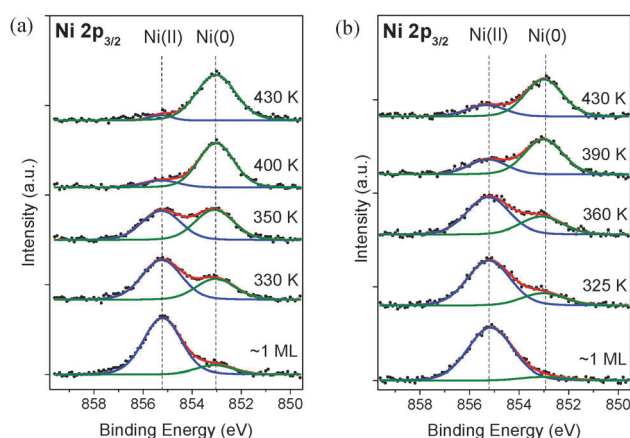
**A Ni–Cu ion exchange has been observed for (5,15-dibromo-10,20-diphenylporphyrinato)nickel(II) (NiDBrDPP) and (5,10,15,20-tetrakis-(4-bromophenyl)porphyrinato)nickel(II) (NiTBrPP) on Cu(111). The ion exchange proceeds at a faster rate for the NiDBrDPP/Cu(111) system compared to NiTBrPP/Cu(111). This is explained in terms of the macrocycle–substrate distance and the distortions that occur when the molecules are deposited on the Cu(111) surface.**

Porphyrins are organic molecules with significant biological and technological functionality.<sup>1</sup> They can be synthesised in either free base or metallated form with a wide range of substituents,<sup>2</sup> and hence they may be tailored to various applications. As such there has been much interest in creating structured porphyrin layers on surfaces, for example covalently bonded porphyrin nano-networks.<sup>3–5</sup> One area of current interest is *in situ* modification of porphyrin molecules on surfaces. In particular, there are several recent studies of metallation of free base porphyrin molecules on surfaces through co-deposition of metal atoms.<sup>6–8</sup> The first reported metallation of a free base porphyrin molecule by substrate atoms was for free base 5,10,15,20-tetrabromophenylporphyrin (H<sub>2</sub>TBrPP) on the Cu(111) substrate.<sup>9</sup> Subsequent papers have reported the metallation of free base tetraphenylporphyrin molecules by substrate atoms.<sup>10–12</sup> However, to our knowledge the *in situ* modification of an already-metallated porphyrin macrocycle whereby the original metal ion is replaced with

a different metal has not been observed before under UHV conditions. Here it is shown that Ni-metallated porphyrins interact with the Cu(111) substrate leading to an exchange of the Ni(II) ion in the macrocycle with a substrate Cu atom, resulting in Cu-metallated porphyrins and metallic nickel atoms on the surface.

X-ray photoemission (XPS) measurements were performed using a lab-based Omicron XPS system as well as at the D1011 beamline, MAX-lab and the SX-700 beamline, ISA. X-ray absorption (XA) measurements were performed at the D1011 beamline. The porphyrin monolayers were prepared *in situ* by thermal evaporation of powder material onto clean Cu(111). The porphyrins studied in this work were synthesized according to published procedures.<sup>3</sup>

Fig. 1(a) and (b) show a series of Ni 2p<sub>3/2</sub> core level XPS spectra for approximately 1 monolayer (ML) of NiDBrDPP and NiTBrPP respectively. The molecules were deposited on Cu(111) at room temperature (RT) and then sequentially annealed at each of the temperatures shown for 45 minutes. For both NiDBrDPP and NiTBrPP the data for the as-deposited layer show two components – a high binding energy component at 855.2 eV assigned to nickel in the Ni(II) oxidation state,<sup>13</sup> and a lower binding energy



**Fig. 1** Ni 2p<sub>3/2</sub> XPS for 1 ML of NiDBrDPP (a) and NiTBrPP (b) on Cu(111) measured at  $h\nu = 1253.6$  eV after deposition at RT and annealing at temperatures shown.

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<sup>†</sup> Electronic supplementary information (ESI) available: Molecular structures, C 1s and N 1s XPS data for NiDBrDPP and NiTBrPP, and van't Hoff plots generated using NiDBrDPP and NiTBrPP Ni 2p<sub>3/2</sub> XPS data shown in Fig. 1. See DOI: 10.1039/c3cc48913b

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component at 853.0 eV, assigned to nickel in the Ni(0) oxidation state.<sup>14</sup> With increasing temperature, the Ni(II) component for both molecules decreases in intensity, with a corresponding increase in the intensity of the Ni(0) component. The total Ni intensity recorded after annealing the NiDBrDPP and NiTBrPP molecular layers at 430 K is approximately 80% and 75%, respectively, of the Ni intensity recorded after initial deposition of the molecule. The intensity of the corresponding C 1s core level for both molecules shows no attenuation (see ESI<sup>†</sup>), indicating that molecules are not desorbed from the surface during annealing. A possible explanation for the attenuation of the Ni signal is the adsorption of the metallic Ni atoms on the Cu surface beneath the porphyrin layers. The presence of a Ni(0) component in the spectra shown in Fig. 1 indicates that Ni atoms have been displaced from the porphyrin macrocycle. Furthermore, it is evident that this process begins at RT on the Cu(111) surface. In addition, a single peak has been observed in the N 1s XPS for the molecules after deposition and during anneal (see ESI<sup>†</sup>). This confirms that the molecules remain metallated at all stages of the experiment, which can only be achieved by incorporation of a surface Cu atom into the porphyrin macrocycle while the Ni(II) ion is displaced from it. This metallation of the macrocycle by surface Cu atoms is not unexpected, given the previous observation of the metallation of free base porphyrins by Cu atoms.<sup>9</sup>

To further investigate the energetics of this exchange reaction, NiDBrDPP and NiTBrPP were deposited on Cu(111) at RT and then repeatedly annealed at 373 K in order to follow the evolution of the Ni signal. The Ni 2p<sub>3/2</sub> core level XPS spectra for NiDBrDPP and NiTBrPP are shown in Fig. 2(a) and (b), respectively, while Fig. 2(c) and (d) show the normalised intensities of the Ni(II) and Ni(0) components as a function of time. The time dependence of the Ni(II) intensity for NiDBrDPP shows an exponential decay with a time constant of 5.5 minutes (Fig. 2(c)), while the Ni(II) intensity for NiTBrPP exhibits an exponential decay with a time constant of 11.6 minutes (Fig. 2(d)). The NiDBrDPP/Cu(111) system reaches a steady state after annealing at 373 K for 25 minutes, with 70% of the Ni atoms in the Ni(0) oxidation state (Fig. 2(a) and (c)), while the NiTBrPP/Cu(111) system reaches a steady state after 40 minutes, with 60% of the Ni atoms in the Ni(0) oxidation state (Fig. 2(b) and (d)). Hence the ion exchange proceeds at a slower rate for NiTBrPP than for NiDBrDPP, indicating the presence of a larger energy barrier for NiTBrPP/Cu(111) than for NiDBrDPP/Cu(111). This difference in exchange rate likely arises due to the Br positions in each molecule. The interaction between the Cu substrate and the Br atoms bonded directly to the *meso* carbon atoms of NiDBrDPP may cause a reduced macrocycle–substrate distance for NiDBrDPP/Cu(111). It has been shown that the phenyl rings of tetraphenyl porphyrin molecules adsorbed on a surface tend to rotate with respect to the macrocycle.<sup>10,15</sup> Such a rotation of the phenyl rings of NiTBrPP would cause an increased macrocycle–substrate separation for NiTBrPP/Cu(111). A larger macrocycle–substrate distance for NiTBrPP compared to NiDBrDPP would result in a larger energy barrier and a slower exchange rate, as is observed. As the NiDBrDPP and NiTBrPP molecular systems reach a steady state after 25 and 40 minutes, respectively, it is assumed that the spectra shown in Fig. 1(a)

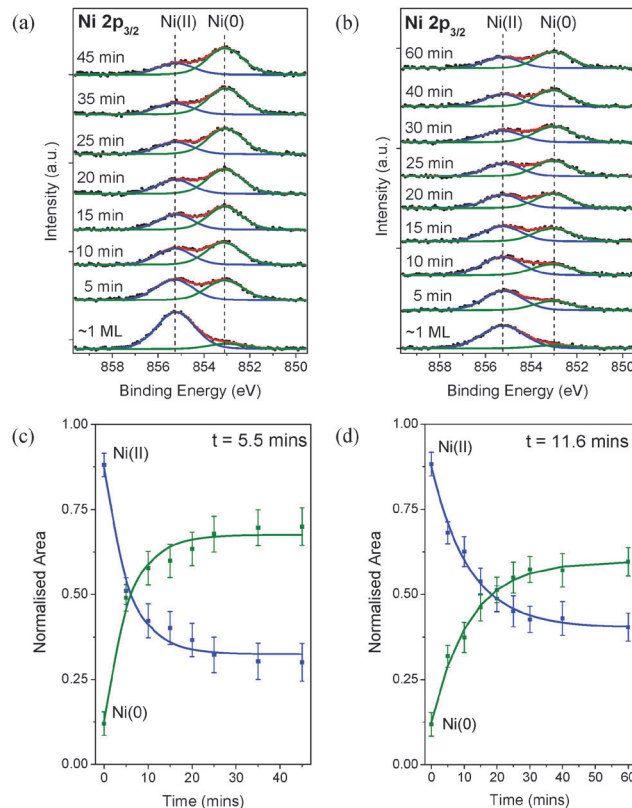


Fig. 2 Ni 2p<sub>3/2</sub> XPS measured at  $h\nu = 1253.6$  eV for (a) 1 ML of NiDBrDPP on Cu(111), deposited at RT and annealed at 373 K for a total of 45 minutes, (b) 1 ML of NiTBrPP on Cu(111), deposited at RT and annealed at 373 K for a total of 60 minutes. (c) and (d) Normalised areas of Ni(II) and Ni(0) peaks as a function of annealing time measured from (a) and (b), respectively.

and (b), recorded after annealing for 45 minutes, correspond to a dynamic equilibrium state of each system.

Fig. 3(a) and (b) show Ni L<sub>3</sub> XA spectra for NiDBrDPP and NiTBrPP, measured after deposition on Cu(111) at RT and subsequent annealing at 510 K and 580 K, respectively. The Ni L<sub>3</sub> XA spectra for both molecules measured after deposition exhibit a main peak, B, at 854.3 eV accompanied by a shoulder, C, at 856.2 eV, which are characteristic for a nickel atom in the porphyrin macrocycle.<sup>16</sup> The low-energy shoulder, A, in each spectrum is due to the presence of the Ni(0) component. This indicates that the exchange reaction on the Cu(111) surface begins at RT for both molecules, in agreement with the Ni 2p<sub>3/2</sub> XPS results (Fig. 1). The Ni L<sub>3</sub> XA spectra recorded after annealing the molecular layers to 510 K and 580 K, respectively, show a sharp onset with an intense peak, A, at 853.1 eV and an asymmetric profile characteristic of metallic nickel.<sup>17</sup> The energy difference of 1.2 eV measured between the Ni(II) and Ni(0) absorption edges is in good agreement with previously reported values.<sup>17</sup> The metallic character of the Ni present on the Cu(111) substrate after annealing the NiDBrDPP and NiTBrPP samples to 510 K and 580 K, respectively, is further evidence that the Ni ions have been displaced from the porphyrin macrocycle. However, the presence of the structures B and C in each annealed spectrum in Fig. 3 indicates that some fraction of the molecules remain unchanged

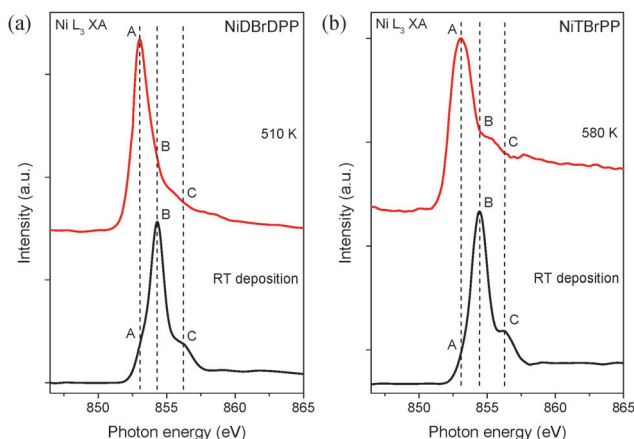
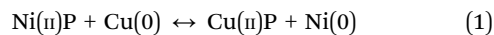


Fig. 3 Ni  $L_3$  XA for 1 ML of NiDBrDPP (a) and NiTBrPP (b) on Cu(111), measured after deposition at RT and annealing at temperatures shown.

after annealing, which is also in agreement with the Ni  $2p_{3/2}$  XPS results (Fig. 1).

The intensities of the Ni components following annealing at different temperatures have been used to analyse the energetics of the Ni–Cu ion exchange. As the spectra shown in Fig. 1 correspond to equilibrium states, a van't Hoff plot<sup>18</sup> can be used to calculate the reaction enthalpy and change in entropy for each of the molecular systems. The Ni–Cu exchange reaction can be expressed as follows:



The equilibrium constant for the reaction is given by

$$K = \frac{[\text{Cu(II)P}][\text{Ni(0)}]}{[\text{Ni(II)P}][\text{Cu(0)}]} = \frac{[1 - \text{Ni(II)P}][\text{Ni(0)}]}{[\text{Ni(II)P}]} \quad (2)$$

where the concentration of surface Cu atoms is in large excess relative to the Ni porphyrin molecules and can be considered constant throughout the exchange reaction, and the concentrations have been normalised to the initial concentration of Ni porphyrins.

The intensities of the Ni(II) and Ni(0) peaks in Fig. 1(a) and (b) can then be used to calculate the equilibrium constant at each anneal temperature. The relationship between the equilibrium constant,  $K$ , and temperature,  $T$ , is given by the van't Hoff equation

$$\ln K = -\frac{\Delta_r H}{RT} + \frac{\Delta S}{R} \quad (3)$$

where  $\Delta_r H$  is the reaction enthalpy,  $\Delta S$  is the change in the entropy and  $R$  is the gas constant,  $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ . Plots of  $\ln K$  as a function of  $1/T$  for both NiDBrDPP and NiTBrPP are shown in the ESI†. The negative slope indicates that the Ni–Cu exchange is an endothermic reaction. From these data the reaction enthalpy  $\Delta_r H$  is calculated as  $50 \pm 2 \text{ kJ mol}^{-1}$  and  $49 \pm 5 \text{ kJ mol}^{-1}$  for NiDBrDPP and NiTBrPP, respectively. The change in the entropy,  $\Delta S$ , is  $141 \pm 8 \text{ J mol}^{-1} \text{ K}^{-1}$  and  $125 \pm 17 \text{ J mol}^{-1} \text{ K}^{-1}$  for NiDBrDPP and NiTBrPP, respectively. As the reaction enthalpy is the same for each system within experimental error, the difference between the two molecular systems is likely due to entropic contributions. Such contributions may be due to distortions of the macrocycle and rotation of the phenyl rings of the molecules. It has been shown

that for CuTPP on Cu(111) the phenyl rings exhibit a rotation angle of  $40\text{--}50^\circ$ .<sup>10</sup> Similar rotation of phenyl substituents has been observed for porphyrins on other metallic surfaces.<sup>15</sup> In addition, saddling and ruffling of the pyrrole rings of porphyrins in general,<sup>2a</sup> and Ni porphyrins in particular,<sup>19</sup> have been reported. Such distortions will be factors in determining the entropy of each system.

In summary, a Ni–Cu exchange reaction has been observed for NiDBrDPP and NiTBrPP molecules on Cu(111), resulting in the incorporation of a surface Cu atom into the porphyrin macrocycle during annealing of molecular layers. In turn, the Ni(II) ions have been displaced from the porphyrin macrocycle and observed as metallic Ni(0) atoms on the copper surface.

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